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(54) Title: COMPOSITE ION EXCHANGE MATERIAL

(57) Abstract: A composite material, for example a composite membrane for a polymer electrolyte membrane fuel cell includes a first conductive polymer and a support material for the polymer, wherein the support material comprises a second conductive polymer. A method making of the composite material is also disclosed as is its use as a polymer electrolyte membrane in a fuel cell.

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external circuit causes an electrical current to flow in the circuit and withdraw electrical power from the cell.

The PEM 2 could comprise a single layer of ion-conducting material. However, in many cases, a single layer of material does not have satisfactory mechanical properties.

Many proposals have been made for improving the mechanical and other properties of ion-conducting materials for as PEMs. For example, US 5834566 (Hoechst) solves the problem by providing homogenous polymer alloys based on sulphonated polyether ketones, whereby the absorption capacity for water and mechanical properties can be adjusted in a controlled manner by varying the components in the alloy and their respective ratios.

It is an object of the present invention to address problems associated with Polymer Electrolyte Membranes.

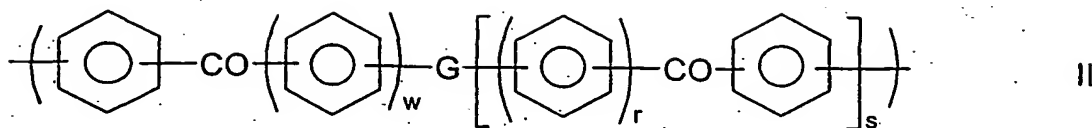
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According to a first aspect of the invention, there is provided a composite material, for example a composite membrane, which includes a first conductive polymer and a support material for the polymer, wherein the support material comprises a second conductive polymer.

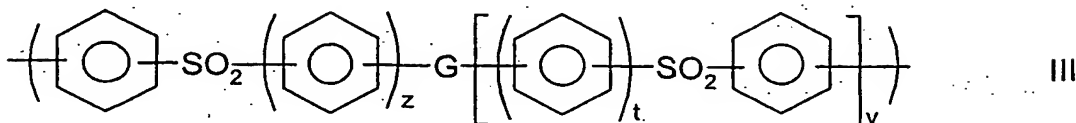
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Said first conductive polymer may comprise a thermoplastic or thermoset aromatic polymer, a polybenzazole or a polyaramid polymer, a perfluorinated ionomer, each of which has been functionalised to provide ion-exchange sites; polystyrene sulfonic acid (PSSA), polytrifluorostyrene sulfonic acid (such as those prepared from alpha, beta, beta-trifluorostyrenes as described in

30



and/or a moiety of formula



5

wherein at least some of the units I, II and/or III are functionalized to provide ion-exchange sites; wherein the phenyl moieties in units I, II, and III are independently
 10 optionally substituted and optionally cross-linked; and wherein m, r, s, t, v, w and z independently represent zero or a positive integer, E and E' independently represent an oxygen or a sulphur atom or a direct link, G represents an oxygen or sulphur atom, a direct link or a -O-Ph-O- moiety
 15 where Ph represents a phenyl group and Ar is selected from one of the following moieties (i)* or (i) to (x) which is bonded via one or more of its phenyl moieties to adjacent moieties

20

group which can be readily elaborated by existing methods to generate $-\text{OSO}_3\text{H}$ and $-\text{OPO}_3\text{H}_2$ cationic exchange sites on the polymer. Ion exchange sites of the type stated may be provided as described in WO95/08581.

5

Preferably, said first conductive polymer is sulphonated. Preferably, the only ion-exchange sites of said first conductive polymer are sites which are sulphonated.

10

References to sulphonation include a reference to substitution with a group $-\text{SO}_3\text{M}$ wherein M stands for one or more elements selected with due consideration to ionic valencies from the following group: H, NR_4^{Y+} , in which R^Y stands for H, $\text{C}_1\text{-C}_4$ alkyl, or an alkali or alkaline earth metal or a metal of sub-group 8, preferably H, NR_4^+ , Na, K, Ca, Mg, Fe, and Pt. Preferably M represents H. Sulphonation of the type stated may be provided as described in WO96/29360.

20

Unless otherwise stated in this specification, a phenyl moiety may have 1,4- or 1,3-, especially 1,4-, linkages to moieties to which it is bonded.

25

Said first conductive polymer may include more than one different type of repeat unit of formula I; more than one different type of repeat unit of formula II; and more than one different type of repeat unit of formula III.

30

Said moieties I, II and III are suitably repeat units. In the polymer, units I, II and/or III are suitably bonded to one another - that is, with no other atoms or groups being bonded between units I, II, and III.

However, for first conductive polymers according to the inventions described herein which are crystalline (which some are) there may be no need to effect cross-linking to produce a material which can be used as a polymer electrolyte membrane. Such polymers may be easier to
5 prepare than cross-linked polymers. Thus, said first conductive polymer of the inventions described herein may be crystalline. Preferably, said polymer is not optionally cross-linked as described.

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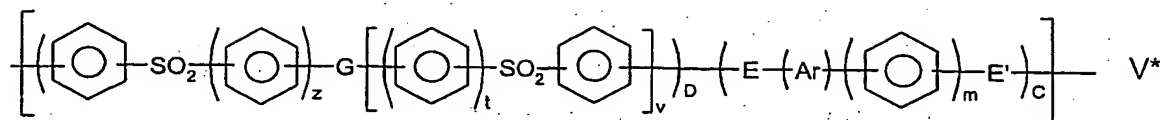
Where w and/or z is/are greater than zero, the respective phenylene moieties may independently have 1,4- or 1,3-linkages to the other moieties in the repeat units of formulae II and/or III. Preferably, said phenylene
15 moieties have 1,4- linkages.

Preferably, the polymeric chain of the polymer does not include a -S- moiety. Preferably, G represents a direct link.

20

Suitably, "a" represents the mole % of units of formula I in said polymer, suitably wherein each unit I is the same; "b" represents the mole % of units of formula II in said polymer, suitably wherein each unit II is the same;
25 and "c" represents the mole % of units of formula III in said polymer, suitably wherein each unit III is the same. Preferably, a is in the range 45-100, more preferably in the range 45-55, especially in the range 48-52. Preferably, the sum of b and c is in the range 0-55, more
30 preferably in the range 45-55, especially in the range 48-52. Preferably, the ratio of a to the sum of b and c is in the range 0.9 to 1.1 and, more preferably, is about 1. Suitably, the sum of a, b and c is at least 90, preferably

or a homopolymer having a repeat unit of general formula



5 or a random or block copolymer of at least two different units of IV* and/or V*, wherein A, B, C, and D independently represent 0 or 1 and E, E', G, Ar, m, r, s, t, v, w and z are as described in any statement herein.

10 Preferably, m is in the range 0-3, more preferably 0-2, especially 0-1. Preferably, r is in the range 0-3, more preferably 0-2, especially 0-1. Preferably t is in the range 0-3, more preferably 0-2, especially 0-1. Preferably, s is 0 or 1. Preferably v is 0 or 1.
 15 Preferably, w is 0 or 1. Preferably z is 0 or 1.

Preferably Ar is selected from the following moieties (xi)* and (xi) to (xxi):

Preferably, (xv) is selected from a 1,2-, 1,3-, or a 1,5- moiety; (xvi) is selected from a 1,6-, 2,3-, 2,6- or a 2,7- moiety; and (xvii) is selected from a 1,2-, 1,4-, 1,5-
5 , 1,8- or a 2,6- moiety.

One preferred class of first conductive polymers may include at least some ketone moieties in the polymeric chain. In such a preferred class, the polymer preferably
10 does not only include -O- and -SO₂- moieties between aryl (or other unsaturated) moieties in the polymeric chain. Thus, in this case, suitably, a polymer of the first and/or second aspects does not consist only of moieties of formula III, but also includes moieties of formula I and/or II.

15

One preferred class of first conductive polymers does not include any moieties of formula III, but suitably only includes moieties of formulae I and/or II. Where said polymer is a homopolymer or random or block copolymer as
20 described, said homopolymer or copolymer suitably includes a repeat unit of general formula IV. Such a polymer may, in some embodiments, not include any repeat unit of general formula V.

25

Suitable moieties Ar are moieties (i)*, (i), (ii), (iv) and (v) and, of these, moieties (i)*, (i), (ii) and (iv) are preferred. Preferred moieties Ar are moieties (xi)*, (xi), (xii), (xiv), (xv) and (xvi) and, of these, moieties (xi)*, (xi), (xii) and (xiv) are especially preferred.

30

Another preferred moiety is moiety (v), especially, moiety (xvi). In relation, in particular to the alternative polymers comprising units IV* and/or V*, preferred Ar moieties are (v) and, especially, (xvi).

Preferred first conductive polymers are copolymers comprising, preferably consisting essentially of, a first repeat unit which is selected from those described below:

5 (a) a unit of formula IV wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m and s represent zero, w represents 1 and A and B represent 1;

10 (b) a unit of formula IV wherein E represents an oxygen atom, E' represents a direct link, Ar represents a moiety of structure (i), m represents zero, A represents 1, B represents zero;

15 (c) a unit of formula V wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m and v represent zero, z represents 1 and C and D represent 1;

20 (d) a unit of formula V wherein E represents an oxygen atom, E' represents a direct link, Ar represents a moiety of structure (ii), m represents 0, C represents 1, D represents 0; or

25 (e) a unit of formula V wherein E and E' represents an oxygen atom, Ar represents a structure (i), m represents 0, C represents 1, Z represents 1, G represents a direct link, v represents 0 and D represents 1;

30 Other preferred first repeat units include:

 (aa) a unit of formula IV wherein E represents an oxygen atom, E' represents a direct link, Ar represents a

link, Ar represents a moiety of structure (iv); m and v represent zero, z represents 1, C and D represent 1;

Other second units which may form copolymers with any
5 of said first repeat units (a) to (e) (and/or with units (aa), (bb) and (cc)) above include: a unit of formula IV wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (v), m represents 0, w represents 1, s represents 0, A and B
10 represent 1; or a unit of formula V wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (v), m represents 0, z represents 1, v represents 0, C and D represent 1.

15 Preferred first conductive polymers for some situations may comprise first units selected from (a), (b), (c) and (e) and second units selected from (f), (g), (h) or (i). A polymer comprising units (d) and (h) may also be preferred. In some situations, first units may be selected from (aa),
20 (bb) and (cc) and second units selected from (f), (g), (h) or (i).

More preferred first conductive polymers are copolymers having a first repeat unit selected from those described
25 above, especially repeat units (b), (d) or (e) in combination with a second repeat unit selected from units (f) or (h). Other particularly preferred polymers are copolymers having a first repeat unit selected from (aa) and (bb) in combination with a second repeat unit selected
30 from units (f) or (h).

In some situations, a difficult to sulphonate unit may include at least one relatively strongly electron-

Copolymers may be prepared having one or more first repeat units and one or more of said second repeat units.

Said copolymers may be random or block copolymers.

5

Where said first conductive polymer is a copolymer as described, the mole% of co-monomer units, for example said first and second repeat units described above, may be varied to vary the solubility of the polymer in solvents, for example in organic solvents which may be used in the preparation of films and/or membranes from the polymers and/or in other solvents, especially water.

One class of first conductive polymers may comprise homopolymers, examples of which include sulphonated polyetheretherketone, polyetherketone, polyetherketoneketone, polyetheretherketoneketone, polyetherketoneetherketoneketone, polyetherdiphenyletherketone and polyether-napthalene-ether-phenyl-ketone-phenyl.

Preferred first conductive polymers suitably have a solubility of at least 10% w/v, preferably a solubility in the range 10 to 30 %w/v in a polar aprotic solvent, for example NMP, DMSO or DMF. Preferred polymers are substantially insoluble in boiling water.

First units of the type described above (with the exception of units (a) and (c)) may be relatively difficult to sulphonate, whereas second units of the type described may be easier to sulphonate.

solution of polymer in concentrated sulphuric acid of density 1.84gcm^3 , said solution containing 0.1g of polymer per 100cm^3 of solution.

5 The measurements of both RV and IV both suitably employ a viscometer having a solvent flow time of approximately 2 minutes.

10 The main peak of the melting endotherm (T_m) for said polymer (if crystalline) may be at least 300°C .

15 In general terms, said first conductive polymer is preferably substantially stable when used as a PEM in a fuel cell. Thus, it suitably has high resistance to oxidation, reduction and hydrolysis and has very low permeability to reactants in the fuel cell. Preferably, however, it has a high proton conductivity. Furthermore, it suitably has high mechanical strength and is capable of being bonded to other components which make up a membrane
20 electrode assembly.

25 Said first conductive polymer may comprise a film, suitably having a thickness of less than 1mm, preferably less than 0.5mm, more preferably less than 0.1mm, especially less than 0.05 mm. The film may have a thickness of at least $5\mu\text{m}$.

30 Said polymer electrolyte membrane may comprise one or more layers wherein, suitably, at least one layer comprises a film of said polymer. Said membrane may have a thickness of at least $5\mu\text{m}$ and, suitably, less than 1mm, preferably less than 0.5mm, more preferably less than 0.1mm, especially less than 0.05mm.

Said second conductive polymer may be selected from any of the materials described above for said first conductive polymer. Preferably, said second conductive polymer is not simply surface sulphonated but the bulk of the material is sulphonated. Thus, the concentration of ion-exchange sites is preferably not concentrated at the surface of the material but are distributed substantially throughout the material. Consequently, it is preferred to prepare said second conductive material (ie incorporating said ion-exchange sites) and then form said material into a support material, for example by casting.

The second conductive material may be distinguished from surface sulphonated materials by the conductivity. Suitably, said second conductive material has an EW of less than 2000, preferably less than 1600, more preferably less than 1200, especially less than 1000. In some cases, EW may be less than 800, 600 or even 500.

In some cases, said second conductive material may have relatively low conductivity, for example EW about 1500. In other cases, the conductivity of said second conductive material may be relatively high (e.g. EW about 300). Thus, preferably, the EW of said second conductive material is in the range 300 - 1500. More preferably, it is in the range 400 - 1000.

Said second conductive polymer preferably has at least some crystallinity - that is, it is preferably semi-crystalline.

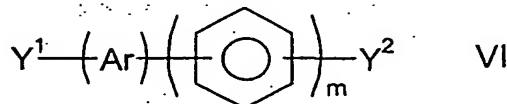
The existence and/or extent of crystallinity in a polymer is preferably measured by wide angle X-ray

Said support material may comprise at least 30wt%, suitably at least 45wt%, preferably at least 50wt%, more preferably at least 75wt%, especially at least 95wt% of said second conductive polymer. Said support material may consist essentially of said second conductive polymer. Alternatively, said support material may comprise a blend of polymers wherein more than one type of conductive polymer is provided in the blend or a blend may include a conductive polymer of the type described and a non-conductive polymer. Examples of non-conductive polymers include polyaryletherketones and polyarylethersulphones, with specific examples being polyetheretherketone, polyetherketone and polyethersulphone.

Said composite membrane suitably incorporates a catalyst material, preferably a layer of a catalyst material which is suitably a platinum catalyst (e.g. platinum containing catalyst) or a mixture of platinum and ruthenium, on both sides of the composite membrane. Electrodes may be arranged outside the catalyst material.

Polymers having units I, II, III, IV, IV*, V and/or V* may be prepared by:

(a) polycondensing a compound of general formula



(c) optionally copolymerizing a product of a process as described in paragraph (a) with a product of a process as described in paragraph (b);

5 wherein the phenyl moieties of units VI, VII and/or VIII are optionally substituted; the compounds VI, VII and/or VIII are optionally sulphonated; and Ar, m, w, r, s, z, t, v, G, E and E' are as described above except that E and E' do not represent a direct link;

10

the process also optionally comprising sulphonating and/or cross-linking a product of the reaction described in paragraphs (a), (b) and/or (c) to prepare said polymer.

15 In some situations, the polymer prepared, more particularly phenyl groups thereof, may be optionally substituted with the groups hereinabove described after polymer formation.

20 Preferably, where Y^1 , Y^2 , X^1 and/or X^2 represent a halogen, especially a fluorine atom, an activating group, especially a carbonyl or sulphone group, is arranged ortho- or para- to the halogen atom.

25 Preferred halogen atoms are fluorine and chlorine atoms, with fluorine atoms being especially preferred. Preferably, halogen atoms are arranged meta- or para- to activating groups, especially carbonyl groups.

30 Where the process described in paragraph (a) is carried out, preferably one of Y^1 and Y^2 represents a fluorine atom and the other represents an hydroxy group. More preferably in this case, Y^1 represents a fluorine atom and Y^2

is, with single units of one said moiety separated by strings of another moiety or moieties which are not all of the same length) or in irregular succession (that is, with at least some multiple units of one moiety separated by
5 strings of other moieties that may or may not be of equal lengths). The moieties described are suitably linked through ether or thioether groups.

Also, moieties in compounds VI, VII and/or VIII
10 arranged between a pair of spaced apart -O- atoms and which include a -phenyl-SO₂ or -phenyl-CO- bonded to one of the -O- atoms may, in the polymer formed in the polycondensation reaction, be present in regular succession, semi-regular succession or in irregular
15 succession, as described previously.

In any sampled polymer, the chains that make up the polymer may be equal or may differ in regularity from one another, either as a result of synthesis conditions or of
20 deliberate blending of separately made batches of polymer.

Compounds of general formula VI, VII and VIII are commercially available (eg from Aldrich U.K.) and/or may be prepared by standard techniques, generally involving
25 Friedel-Crafts reactions, followed by appropriate derivatisation of functional groups. The preparations of some of the monomers described herein are described in P M Hergenrother, B J Jensen and S J Havens, Polymer 29, 358 (1988), H R Kricheldorf and U Delius, Macromolecules 22,
30 517 (1989) and P A Staniland, Bull, Soc, Chem, Belg., 98 (9-10), 667 (1989).

The method preferably includes the step of contacting the support material with a first solvent which solubilises, to some degree, the support material. Said solvent may be capable of dissolving the support material to a level of at least 5 wt%. Said solvent is preferably not a polar aprotic organic solvent, such as NMP. Said solvent is preferably a protic solvent. Said solvent preferably comprises or consists essentially of a strong acid solvent. Said solvent may comprise at least 90%, preferably at least 95%, more preferably at least 97%, especially at least 98% acid. Said strong acid solvent may be one or more of sulphuric acid, a sulphonic acid (e.g. methane sulphonic acid, trichloromethane sulphonic acid, trifluoromethane sulphonic acid), hydrofluoric acid and phosphoric acid. Said first solvent and said support material are preferably selected so that said first solvent does not functionalise the support material to provide ion-exchange sites, for example sulphonate groups. Thus, preferably, said first solvent and said support material are selected so that said first solvent does not sulphonate the support material.

In one embodiment, the method may involve said support material, suitably comprising sulphonated aromatic ether ketone polymers or copolymers or aromatic ether ketone/ether sulphone copolymers, being dissolved in said first solvent. Then, a second solvent is used to cause pores to be formed in said support material. Next, a solution which includes the first conductive polymer, suitably comprising aromatic ether ketone polymer or copolymer or aromatic ether ketone/ether sulphone copolymer, is contacted with said porous support material. A third solvent used to form the solution of the first

is a component of a blend, another component or components of the blend may be substantially soluble or insoluble in the third solvent. Preferably, said support material is not substantially solubilised by said third solvent.

5 Preferably, said support material is substantially insoluble in said third solvent. Said third solvent is preferably not a strong acid. Said third solvent may be an aprotic solvent, especially a polar aprotic solvent. Said third solvent is preferably organic. It may be an alcohol

10 or a mixture of aprotic solvent and alcohol.

Where said first conductive polymer comprises moieties I, II and/or III described above, said third solvent is preferably a polar aprotic solvent, especially NMP. Where

15 said first conductive polymer is a perfluorinated ionomer then the third solvent may be an alcohol.

The ratio of the EW of the first conductive polymer to the second conductive polymer may be in the range 0.5 to 2.

20

In one embodiment, the method may involve said support material, suitably comprising polyetheretherketone, polyetherketone, polyetheretherketoneketone, polyetherketoneketone or polyetherketoneetherketoneketone,

25 sulphonated to a level at which they do not swell excessively in water, being dissolved in said first solvent. Then, the second solvent is used to cause pores to be formed in said support material. Next, a solution of the first conductive polymer, (which may be any of the

30 first conductive polymers described herein, but preferably includes moieties I, II or III described above and may be polyetheretherketone, polyetherketone, polyetheretherketoneketone, polyetherketoneketone or

act as a "Reverse Osmosis" membrane, allowing the passage of protons and water, but preventing the passage of organic molecules, such as methanol or hydrocarbons. A composite membrane of such a structure could reduce methanol cross-
5 over in Direct Methanol Fuel Cells.

In an embodiment wherein the support material comprises a blend of polymers, one of which is said second conductive polymer, one of the polymers in the blend may be at least
10 partially soluble in the third solvent which comprises the first conductive polymer. Consequently, the first conductive polymer may penetrate the support material, suitably in regions thereof which are solubilised by the third solvent. By way of example, a support material may be
15 a blend of a second conductive polymer (which is a copolymer of sulphonated etherdiphenyletherketone and etherketone) and polyethersulphone (which is soluble in NMP). The first conductive polymer, dissolved in NMP, may be contacted with the aforesaid support material whereby
20 the polyethersulphone thereof may be dissolved allowing penetration of the first conductive polymer into dissolved regions.

In general terms, wherein the support material
25 comprises a blend of polymers, one of which is said second conductive polymer, said second conductive polymer and the polymer or polymers with which said second conductive polymer is blended are preferably selected so that a said first solvent used to cast the support material does not
30 functionalise the support material to provide ion-exchange sites when contacted therewith. Examples of polymers with which said second conductive polymer may be blended include polyaryletherketones; polyarylethersulphones;

humidity sensors, as the electrical conductivity of an ion exchange membrane varies with humidity.

- 5 5. Ion-exchange material for separations by ion-exchange chromatography. Typical such applications are deionization and desalination of water (for example, the purification of heavy metal contaminated water), ion separations (for example, rare-earth metal ions, trans-uranium elements), and the removal of interfering ionic species.
- 10 6. Ion-exchange membranes employed in analytical preconcentration techniques (Donnan Dialysis). This technique is typically employed in analytical chemical processes to concentrate dilute ionic species to be analysed.
- 15 7. Ion-exchange membranes in electrodialysis, in which membranes are employed to separate components of an ionic solution under the driving force of an electrical current. Electrolysis applications include the industrial-scale desalination of brackish water, preparation of boiler feed make-up and chemical process 20 water, de-ashing of sugar solutions, deacidification of citrus juices, separation of amino acids, and the like.
- 25 8. Membranes in dialysis applications, in which solutes diffuse from one side of the membrane (the feed side) to the other side according to their concentration gradient. Separation between solutes is obtained as a result of differences in diffusion rates across the membrane arising from differences in molecular size. Such applications include hemodialysis (artificial 30 kidneys) and the removal of alcohol from beer.
9. Membranes in gas separation (gas permeation) and pervaporation (liquid permeation) techniques.

Unless otherwise stated, all chemicals referred to hereinafter were used as received from Sigma-Aldrich Chemical Company, Dorset, U.K.

5 Example 1

A 700ml flanged flask fitted with a ground glass Quickfit lid, stirrer/stirrer guide, nitrogen inlet and outlet was charged with 4,4'-difluorobenzophenone (89.03g, 0.408 mole), 4,4'-dihydroxybiphenyl (24.58g, 0.132 mole)
10 4,4'-dihydroxybenzophenone (57.41g, 0.268 mole), and diphenysulphone (332g) and purged with nitrogen for over 1 hour. The contents were then heated under a nitrogen blanket to between 140 and 150°C to form an almost colourless solution. While maintaining a nitrogen
15 blanket, dried sodium carbonate (43.24g, 0.408 mole) was added. The temperature was raised gradually to 315°C over 2 hours then maintained for 1 hours.

The reaction mixture was allowed to cool, milled and
20 washed with acetone and water. The resulting polymer was dried in an air oven at 120°C. The polymer had a melt viscosity at 400°C, 1000sec⁻¹ of 0.54 kNsm⁻².

Example 2

25 A 700ml flanged flask fitted with a ground glass Quickfit lid, stirrer/stirrer guide, nitrogen inlet and outlet was charged with 4,4'-difluorobenzophenone (89.03g, 0.408 mole), 4,4'-dihydroxybiphenyl (18.62g, 0.10 mole)
4,4'-dihydroxybenzophenone (64.26g, 0.30 mole), and
30 diphenysulphone (332g) and purged with nitrogen for over 1 hour. The contents were then heated under a nitrogen blanket to between 140 and 150°C to form an almost colourless solution. While maintaining a nitrogen

0.408 mole), 4,4'-dihydroxybiphenyl (29.79g, 0.16 mole) 4,4'-dihydroxydiphenylsulphone (60.06g, 0.24 mole), and diphenylsulphone (332g) and purged with nitrogen for over 1 hour. The contents were then heated under a nitrogen
5 blanket to between 140 and 150°C to form an almost colourless solution. While maintaining a nitrogen blanket, dried sodium carbonate (43.24g, 0.408 mole) was added. The temperature was raised gradually to 315°C over 3 hours then maintained for 0.5 hours.

10

The reaction mixture was allowed to cool, milled and washed with acetone and water. The resulting polymer was dried in an air oven at 120°C. The polymer had a melt viscosity at 400°C, 1000sec⁻¹ of 0.6 kNsm⁻².

15

Example 5

A 700ml flanged flask fitted with a ground glass Quickfit lid, stirrer/stirrer guide, nitrogen inlet and outlet was charged with 4,4'-dichlorodiphenylsulphone
20 (104.25g, 0.36 mole), 4,4'-dihydroxybiphenyl (22.32g, 0.12 mole) 4,4'-dihydroxydiphenylsulphone (60.06g, 0.24 mole), and diphenylsulphone (245g) and purged with nitrogen for over 1 hour. The contents were then heated under a nitrogen blanket to between 140 and 145°C to form an
25 almost colourless solution. While maintaining a nitrogen blanket, dried potassium carbonate (50.76g, 0.37 mole) was added. The temperature was raised to 180°C, held for 0.5 hours, raised to 205°C, held for 1 hour, raised to 225°C, held for 2 hours, raised to 265°C, held for 0.5 hours,
30 raised to 280°C and held for 2 hours.

The reaction mixture was allowed to cool, milled and washed with acetone/methanol (30/70) and water. The

Example 7 (Preparation of unreinforced membrane)

Membranes were produced from the polymer from Example 4 after sulphonation as described in Example 6 by dissolving the polymer in N-methylpyrrolidone (NMP) at a concentration of 15% w/w. The homogeneous solution was cast onto clean glass plates and then drawn down to give 400 micron films, using a stainless steel Gardner Knife. Evaporation at 100°C under vacuum for 24 hours produced membranes of mean thickness 40 microns.

Example 8 - General procedure for making conductive microporous membranes impregnated with conductive material

A sulphonated polymer (selected from those described in Examples 1 and 2 and sulphonated as described in Example 6) was dissolved in 98% sulphuric acid, (10%w/w) and cast onto a glass plate to produce a 100µm wet thickness coating. The plate was immersed in deionized water, removed, dried under vacuum at 105°C, thereby producing a microporous membrane. This membrane was then impregnated with a 15% (w/w) solution of the polymer prepared as described in Example 4 (and having been sulphonated as described in Example 6) in NMP to produce a wet thickness of the solution of 250µm, followed by drying for 20hrs at 105°C. The membranes prepared from the polymers described in Examples 1 and 2 are hereinafter referred to as Examples 8a and 8b respectively. The unreinforced membrane of Example 7 was highly swollen and fragile after immersion in boiling water for 1 hour, whereas the composite membranes of Examples 8a and 8b were strong and flexible.

removed, dried under vacuum at 105°C, thereby producing a microporous membrane. The membrane was then impregnated with a 5% (w/w) solution of Nafion (Trade Mark) (a perfluorosulphonic acid) in a mixture of lower alcohols and to produce a wet thickness of the solution of 300µm, followed by drying for 20hrs at 105°C. The unreinforced membrane was highly swollen and fragile after immersion in boiling water for 1 hour, whereas the composite membrane was strong and flexible.

Example 11

Polyetherketone (PEK™ -P22, Victrex plc, Melt Viscosity 0.22kNsm⁻²) and the polymer from Example 1 sulphonated as described in Example 6 were separately dissolved in 98% sulphuric acid (7%w/w), blended in a ratio 1:1 then cast onto a glass plate to produce a 150 µm wet thickness coating. The plate was immersed in deionized water, removed, dried under vacuum at 105°C, thereby producing a microporous membrane. This membrane was then impregnated with a 15% (w/w) solution of the polymer prepared as described in Example 4 (and having been sulphonated as described in Example 6) in NMP to produce a wet thickness of the solution of 250µm, followed by drying for 2hrs at 105°C. The wet unreinforced membrane was highly swollen and fragile, whereas the wet composite membrane was strong and flexible, with the boiling water uptake being 520% and 110% respectively.

Example 12

The polymer from Example 1 sulphonated as described in Example 6 was dissolved in 98% sulphuric acid, (10%w/w) and cast onto a glass plate to produce a 100µm wet thickness coating. The plate was immersed in deionized

Example	Sulphonated Impregnating Ion Conducting Membrane wet thickness	Mean Membrane Final dry thickness (microns)	Boiling Water Uptake (%)
Example 13a	300	75	225.00
Example 13b	300.00	40	127
Example 13c	225.00	40	103
Example 7d	525.00	40	520

Example 14 Comparison of Fuel Cell Performance of Reinforced Composite Membrane prepared in Example 8a with Unreinforced Membrane prepared in Example 7.

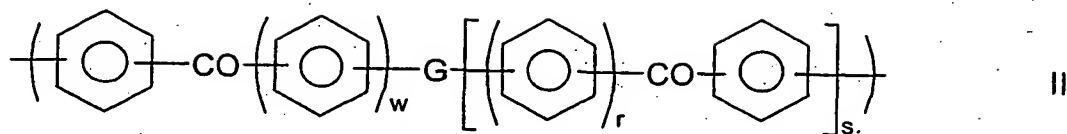
The reinforced composite membrane prepared in Example 8a and the unreinforced membrane prepared in Example 7 were pre-treated by boiling in 1M sulphuric acid, allowed to cool to room temperature followed by thorough washing with deionised water. Membrane Electrode Assemblies (MEA) were prepared using standard platinum loaded, Nafion® impregnated Gas Diffusion Electrodes (E-Tek, Elat 0.35mg Pt cm⁻²) hot pressed onto the membrane. The active area being 11.8cm². The following operating conditions were followed:

Hydrogen Pressure	3Barg
Air Pressure	3Barg
Hydrogen Stoichiometry	1.5
Air Stoichiometry	3
Cell Temperature	60°C
Current Density	0.7Acm ⁻²

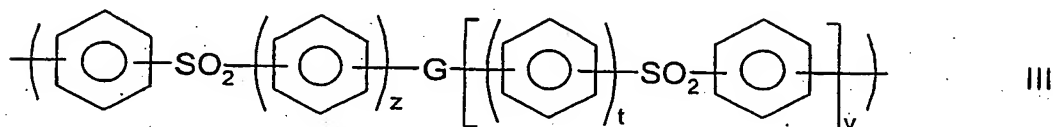
All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive.

Each feature disclosed in this specification (including any accompanying claims, abstract and drawings), may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

The invention is not restricted to the details of the foregoing embodiment(s). The invention extend to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.



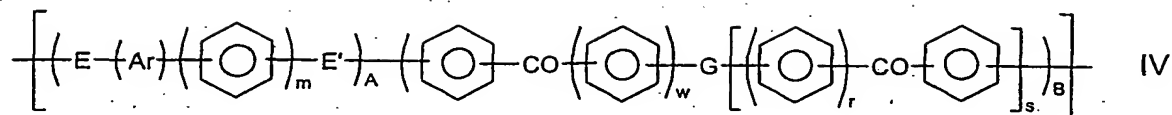
and/or a moiety of formula



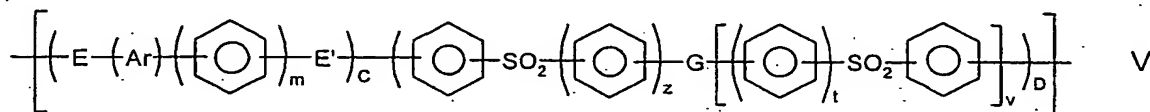
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wherein at least some of the units I, II and/or III are functionalized to provide ion-exchange sites; wherein the phenyl moieties in units I, II, and III are independently
 10 optionally substituted and optionally cross-linked; and wherein m, r, s, t, v, w and z independently represent zero or a positive integer, E and E' independently represent an oxygen or a sulphur atom or a direct link, G represents an oxygen or sulphur atom, a direct link or a -O-Ph-O- moiety
 15 where Ph represents a phenyl group and Ar is selected from one of the following moieties (i)* or (i) to (x) which is bonded via one or more of its phenyl moieties to adjacent moieties

20

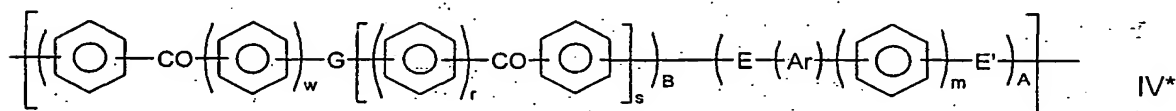


or a homopolymer having a repeat unit of general formula

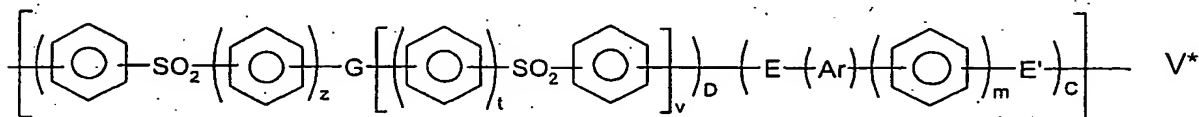


5 or

a homopolymer having a repeat unit of general formula



or a homopolymer having a repeat unit of general formula



10

or a random or block copolymer of at least two different units selected from IV and V or from IV* and V*,

15 wherein A, B, C and D independently represent 0 or 1 and E, E', G, Ar, M, r, s, t, v, w and z are as described in claim 4.

moiety of structure (iv), m and v represent zero, z represents 1 and C and D represent 1;

(d) a unit of formula V wherein E represents an oxygen
5 atom, E' represents a direct link, Ar represents a moiety
of structure (ii), m represents 0, C represents 1, D
represents 0; or

(e) a unit of formula V wherein E and E' represents an
10 oxygen atom, Ar represents a structure (i), m represents 0,
C represents 1, Z represents 1, G represents a direct link,
v represents 0 and D represents 1;

(aa) a unit of formula IV wherein E represents an
15 oxygen atom, E' represents a direct link, Ar represents a
structure (i)*, m represents 0, A represents 1, B
represents 0;

(bb) a unit of formula IV wherein E and E' represent
20 oxygen atoms, Ar represents a structure (iv), m and w
represent 0, G represents a direct link, s and r represent
1, A and B represent 1;

(cc) a unit of formula IV wherein E and E' represent
25 oxygen atoms, Ar represents a structure (i), m and w
represent 0, G represents a direct link, s and r represent
1, A and B represent 1;

and a second repeat unit which is selected from the
30 following:

(f) a unit of formula IV wherein E and E' represent
oxygen atoms, G represents a direct link, Ar represents a

13. A material according to any preceding claim, wherein said first conductive polymer has an equivalent weight (EW) of less than 500g/mol.

5

14. A material according to any preceding claim, wherein said second conductive polymer is selected from a material described for said first conductive polymer in any preceding claim.

10

15. A material according to any preceding claim, wherein said second conductive polymer has an equivalent weight (EW) of less than 2000.

15

16. A material according to any preceding claim, wherein said second conductive polymer is semi-crystalline.

17. A material according to any preceding claim, wherein said composite material incorporates a catalyst material.

20

18. A method of making a composite material, the method comprising causing a first conductive polymer to be associated with a support material which comprises a second conductive polymer, thereby to produce a composite membrane comprising said first conductive polymer and said support material.

25

19. A method according to claim 18, which includes the step of contacting the support material with a first solvent which solubilises the support material.

30

20. A method according to claim 19, which includes contacting the support material with a second solvent

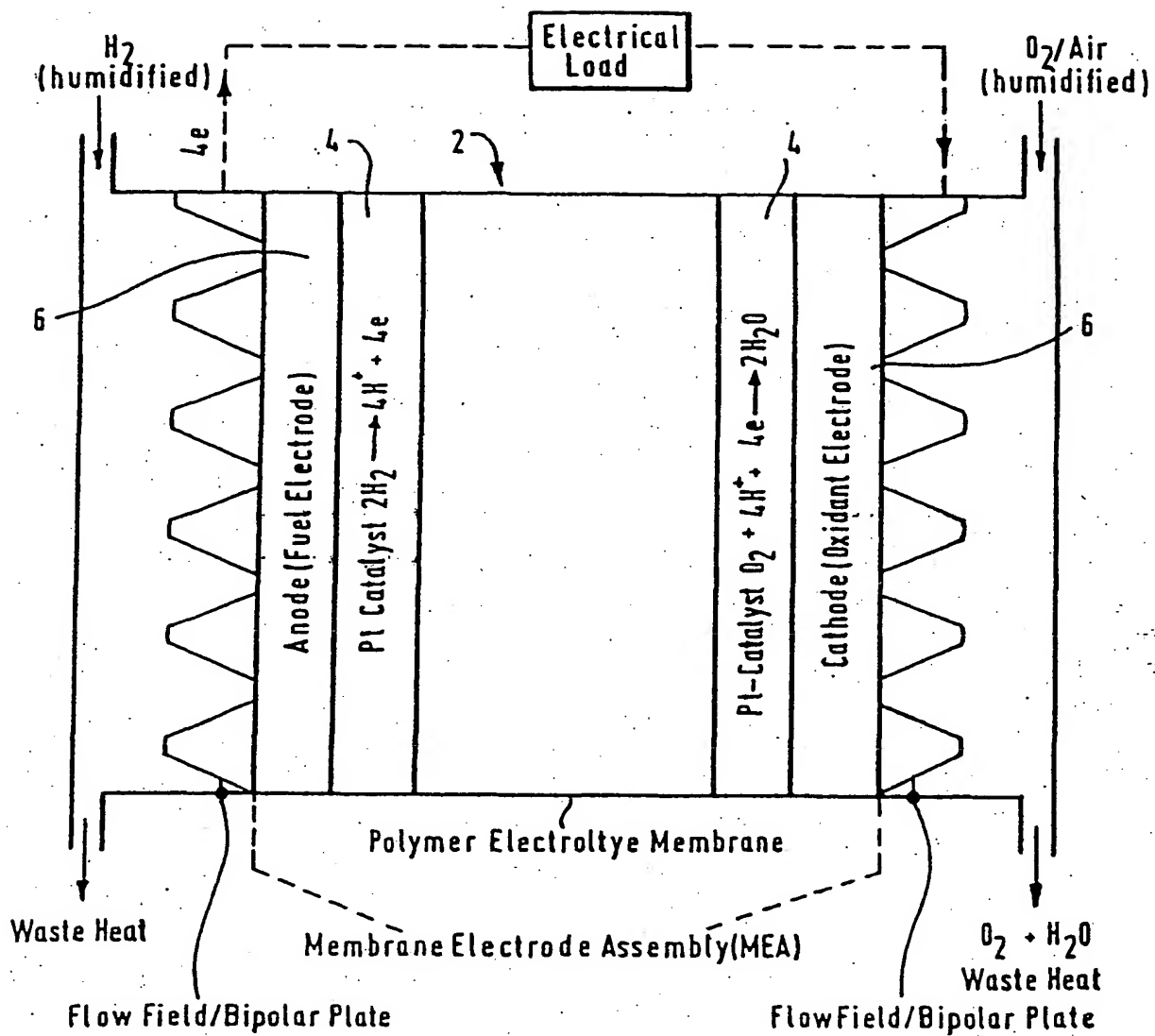


Figure 1

PEI (polyetherimide) R=aryl, alkyl, aryl ether or alkylether	
Udel polysulfone	
Radel R polyphenylsulfone	
Radel A polyethersulfone	
poly(trifluoro-methyl-bis(phthalimide)-phenylene)	
poly(triphenylphosphine oxide sulfide-phenylsulfone-sulfide)	
(PBO-PI) poly(benz(bis)oxazole)	
poly(phenylsulfide 1,4-phenylene)	

Figure 3a

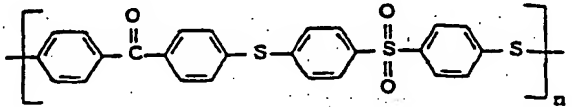
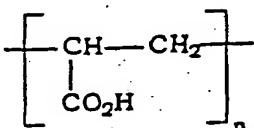
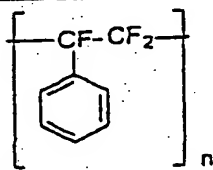
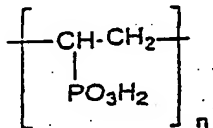
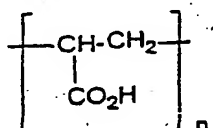
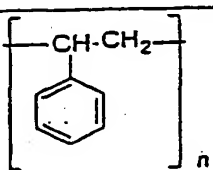
poly(benzophenone sulfide-phenylsulfone-sulfide)	
polyvinyl carboxylic acid	
trifluoro styrene	
polyvinyl phosphonic acid	
polyvinyl carboxylic acid	
polystyrene sulfonic acid (PSSA)	

Figure 3c